^{13}C NMR Spectra of Geometric Isomers of Ring-substituted 1,2-Oxaphosphorinanes

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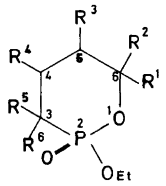
During recent years considerable effort has been expended in ^{13}C NMR studies of various six-membered ring systems containing one or more heteroatoms in the ring.[1-13] As part of our NMR studies on cyclic phosphonates, phosphites and arsenites, we have investigated the ^{13}C NMR spectra of geometric isomers of ring-substituted 1,2-oxaphosphorinanes, I–VI. In earlier papers the preparation, spectral properties and conformational energies of 1,2-oxaphosphorinanes have been published, and the present paper reports the first ^{13}C NMR investigation on these compounds.

Experimental. The syntheses and physical data of the geometric isomers of I to VI have been described in previous papers.[14-18] The isomers were examined in *ca.* 15 % v/v $CDCl_3$ solutions at ambient probe temperature on a BRUKER CXP100 Spectrometer operating at 15.04 and 22.64 MHz. The broad band proton decoupled ^{13}C spectra were run at a spectral width of about 4 KHz and a data memory size of 8 or 16 K depending on the required resolution. The spectra were obtained using 10 mm O.D. sample tubes with internal ^{2}H lock to $CDCl_3$.

Results and discussion. The studied compounds and measured ^{13}C chemical shifts and $^{13}C-^{31}P$ coupling constants are listed in Tables 1 and 2. The ^{13}C chemical shifts were obtained under proton-noise decoupling conditions.

The assignment of the resonance signals due to C(3) and C(6) in the *cis* and *trans* isomers of I, III and V were indentified by comparing their ^{13}C NMR spectra with that of their 3,3,6-trideuterio analogue II and 3,3,6,6-tetradeuterio analogues IV and VI. The signals which were absent in the spectra of the trideuterated and tetradeuterated compounds were assigned to C(3) and C(6) of I, III and V. The assignment of the resonance signals due to C(6) followed also from the downfield inductive effect on the ring oxygen atom and intensity considerations. In order to distinguish between C(4) and C(5) in the studied compounds gated decoupling was employed.

Table 1. ^{13}C NMR chemical shifts (ppm from TMS) for the geometric isomers of 1,2-oxaphosphorinanes measured in deuteriochloroform solution.



Compound	Substituents, R^i [a]	C(3)	C(4)	C(5)	C(6)	4-Me	5-Me	6-Me
I, *cis*	$R^1=Me$	21.51	19.70	32.73	75.47			20.51
I, *trans*	$R^1=Me$	21.89	22.23	32.91	77.10			21.11
II, *cis*	$R^1=Me, R^2=R^5=R^6=D$		19.83	32.59				20.65
II, *trans*	$R^1=Me, R^2=R^5=R^6=D$		22.12	32.74				20.91
III, *cis*	$R^3=Me$	18.64	27.44	29.12	72.64		15.04	
III, *trans*	$R^3=Me$	21.98	29.63	30.80	74.18		15.49	
IV, *cis*	$R^3=Me, R^1=R^2=R^5=R^6=D$		28.27	29.48			15.30	
IV, *trans*	$R^3=Me, R^1=R^2=R^5=R^6=D$		29.55	30.72			15.61	
V, *cis,cis*	$R^3=R^4=Me$	27.17	31.26	33.82	71.31	17.13	10.42	
V, *trans,cis*	$R^3=R^4=Me$	26.07	31.90	33.78	73.63	19.73	8.82	
VI, *cis,cis*	$R^3=R^4=Me, R^1=R^2=R^5=R^6=D$		30.14	32.48		15.95	7.91	
VI, *trans,cis*	$R^3=R^4=Me, R^1=R^2=R^5=R^6=D$		31.95	33.82		20.06	9.23	

[a] $R^i=H$ unless otherwise stated.

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Table 2. $^{31}P-^{13}C$ nuclear spin coupling constants (in H_z) for the geometric isomers of 1,2-oxaphosphorinanes.

Compound	Substituents, R^i [a]	$^1J_{P-C(3)}$	$^2J_{P-C(4)}$	$^3J_{P-C(5)}$	$^2J_{P-C(6)}$	$^3J_{P-R^1}$	$^3J_{P-R^4}$
I, *cis*	$R^1=Me$	128.17	6.83	5.98	5.12	8.54	
I, *trans*	$R^1=Me$	128.17	8.11	5.98	7.29	8.11	
II, *cis*	$R^1=Me, R^2=R^5=R^6=D$		6.75	5.14		7.32	
II, *trans*	$R^1=Me, R^2=R^5=R^6=D$		7.69	5.12		7.69	
III, *cis*	$R^3=Me$	128.17	8.54	7.69	5.12		
III, *trans*	$R^3=Me$	128.17	7.69	7.69	6.79		
IV, *cis*	$R^3=Me, R^1=R^2=R^5=R^6=D$		7.69	6.83			
IV, *trans*	$R^3=Me, R^1=R^2=R^5=R^6=D$		5.98	5.12			
V, *cis,cis*	$R^3=R^4=Me$	125.93	6.01	5.15	5.15		12.98
V, *trans,cis*	$R^3=R^4=Me$	125.93	6.44	4.72	6.44		18.48
VI, *cis,cis*	$R^3=R^4=Me, R^1=R^2=R^5=R^6=D$		5.98	4.25			11.96
VI, *trans,cis*	$R^3=R^4=Me, R^1=R^2=R^5=R^6=D$		5.98	5.12			18.79

[a] $R^i=H$ unless otherwise stated.

The signal with greater multiplicity was assigned to C(5) and was the more deshielded in I and II. For the assignment of the methyl signals off-resonance decoupling together with empirically established trends of methyl substitution on carbon resonance were employed.[3,19,20]

Previous IR and ^1H NMR investigations[14-18] have shown that the 1,2-oxaphosphorinane ring in the *cis* and *trans* isomer of I and II, the *trans* isomer of III and the 2,4-*trans*, 4,5-*cis*-isomer of V and VI exist in a rigid chair conformation with an equatorial methyl group in position 6 in I, II and the 2,4-*trans*-4,5-*cis* isomers of V and VI and in position 5 of the *trans* isomer of III. In these compounds the preferred orientation of the phosphoryl group is equatorial. However, in the *cis* isomers of III and in the 2,4-*cis*-4,5-*cis*-isomer of V and VI the 1,2-oxaphosphorinane ring undergoes rapid equilibration between two conformers, and the ring inversion ought to cause conformational change around the phosphorus atom. The measured ^{13}C chemical shifts and the $^{31}P-^{13}C$ coupling constants are in agreement with the above assumption.

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